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ARL-TR-1930 April 1999

Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

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Abstract

Ferroelectric barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$ [BSTO]) films of 1-µm nominal thickness were deposited on single crystals of sapphire and electroded substrates at substrate temperatures varying from 30” C to 700° C. The microstructure of the thin films was columnar at all substrate deposition temperatures. The film microhardness showed a trend toward increased hardness with substrate temperature. Furthermore, with the elevation in substrate temperature, there was a parallel increase in film-substrate adhesion measurements, while the cohesion measurements were not influenced by substrate temperature.

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1. Introduction

The Army has an active interest in phased-array antennas. In terms of performance, phased-array antennas offer significant advantages over their mechanical counterparts, namely, higher speed, increased accuracy, and higher reliability. Traditionally, phased-array antennas have been constructed using ferrite phase-shifting elements. Due to circuit design requirements, these antennas are large and costly (Sengupta 1996). Future Army requirements will demand antennas that are smaller and lighter with higher performance and greater long-term reliability. Thus, new materials are key elements in realizing this goal and must be developed, evaluated, and optimized for the application. To this end, a barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$ [BSTO]), phase-shifter device employing a planar microstrip construction has been demonstrated as a possible candidate (L. C. Sengupta et al. 1995). Results of this work have clearly shown BSTO to be a reasonable candidate for phase-shifter applications. In an effort to optimize the performance of the material (i.e., to increase the operating frequency [>30 MHz] and lower voltage requirements), thin-film fabrication of BSTO is critical. Thin films of BSTO deposited via pulsed-laser deposition (PLD) have been demonstrated in previous work (S. Sengupta et al. 1995). These films have exhibited excellent electronic properties, including tunable dielectric constants and low electronic loss (Sengupta et al. 1994). However, there has been little investigation into the microstructural and mechanical aspects of these films. Previous work has demonstrated that the microstructure of thin films has a significant influence on device electrical performance and reliability (Ikawa 1993; Cole et al. 1998). Furthermore, it is postulated that thin-film microstructure has a strong influence on its mechanical properties (Garsgin, Lavernova, and Mokhov 1997). The mechanical properties, including internal stresses and adhesion, are important factors affecting the mechanical integrity and reliability of a device constructed of these thin films. Though a film may show superior electronic properties, it is the mechanical properties, along with electrical properties, which permit the film to be useful in a device such as a phased-array antenna. This paper presents the results of an investigation into the effects of substrate temperature during deposition on the mechanical properties as well as microstructure of BSTO thin films.

2. Experimental

Films of 1-μ nominal thickness were deposited via PLD onto single-crystal sapphire and electroded substrates. Prior to deposition, the substrates were ultrasonically cleaned in an isopropyl bath. A 248-nm KrF laser was employed for the deposition of BSTO thin films from source targets. The energy of the laser during deposition was 400 mJ per pulse, with a pulse frequency of 10 Hz and pulse width of 20 ns. The chamber pressure was held at 50 mtorr of oxygen. The laser spot was mechanically scanned across a rotating target to ensure film uniformity and avoid cratering in the target. Target-to-substrate distance was 75 mm. The films were deposited at a constant rate. The temperature of the substrate was varied from 30" C to 700" C via a resistance heater on the substrate mount. Temperature was monitored by a thermocouple imbedded in the heater.

The Knoop microhardness on the free surface of these coatings, uncorrected for substrate hardness effects, was measured using a 0.25-N applied load and a dwell time of 15 s. Even at this low load, the maximum indenter penetration far exceeded the critical value of 1/10 of the coating thickness that is considered to be sufficient for the substrate not to have a significant effect on hardness values. However, since all substrates were identical, all measurements were internally consistent. Thus, while the hardness numbers cannot be taken as absolute, if taken as a set, they do illustrate a trend of increased hardness as substrate temperature increases.

The cohesion and adhesion values of the various coatings were evaluated primarily with a Centre Suisse d'Electronique et de Microtechnique (CSEM)-Revetest (CSEM CH-20007, Neuchâtel, Switzerland) automatic scratch apparatus. The apparatus employed a diamond stylus with a radius of 200 μm. The testing procedures for this experiment are described in Kattamis et al. (1993); Bhansali and Kattamis (1990); Kattamis (1993); and Steimann, Tardy, and Hintermann (1987). The sample translation speed was held constant at 5 mm/min, and the loading rate at 5 N/min; hence, the load gradient was dL/dx = 1 N/mm. The cohesion failure load, L_C, is the minimum crack initiation load within the coating, and the adhesion failure load,

L_A, is the minimum load at which the crack causes massive delamination at the coating/substrate interface.

The fracture cross sections of the films were observed by scanning electron microscopy (SEM) to obtain a rough idea of the microstructure. Cross-sectional transmission electron microscopy (TEM) was performed on the BSTO films to confirm the film's columnar microstructure. Selected-area electron diffraction (SAED) was used to confirm the film's crystallinity. An Amray 1820 SEM with an accelerating voltage of 20 kV was used for surface analysis. The JEOL 3010 transmission electron microscope with scanning attachment and operating voltage of 300 kV was used to perform the cross-sectional TEM and SAED.

3. Results and Discussion

The microstructure of the BSTO thin film, at various substrate temperatures, was evaluated by SEM and TEM. Figure 1 shows a fracture cross section of the BSTO film substrate. From Figure 1, the columnar structure of the films can be classified as being in the Thornton (1977) structural zone 2.

Figure 2 is a cross-sectional TEM micrograph of BSTO. The figure illustrates the dense polycrystalline nature of the film and the columnar grain structure. There was no evidence of microporosity at the boundaries or in the grain interiors. Also, note the different orientations of the columnar grains. This can be attributed to the uneven surface of the substrate. Figure 2 further supports the point that these films are of the Thornton structural zone 2 type. Zone 2 consists of dense columnar grains with growth as the result of surface recrystallization and surface diffusion. It is well known that the substrate temperature, T_s; the ambient gas pressure; and the energy of any incoming ions influence the growth conditions and, therefore, the film structure produced under low-pressure conditions (Movchan and Demchishin 1969; Thornton 1977; Fountzoulas and Nowak 1991). A structural classification system that has gained the broad acceptance for thin films produced by physical vapor deposition (PVD) process has been

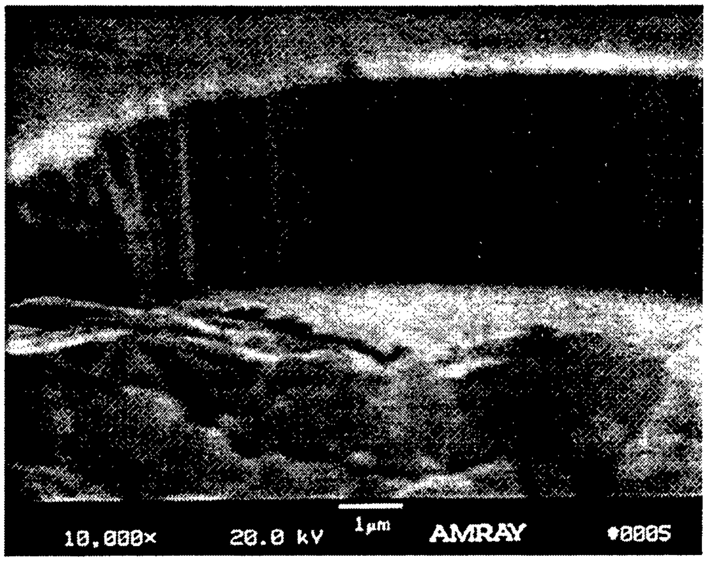

Figure 1. Scanning Electron Photomicrograph of a Fracture Cross Section of a BSTO Film ($T_s/T_m = 0.15$).

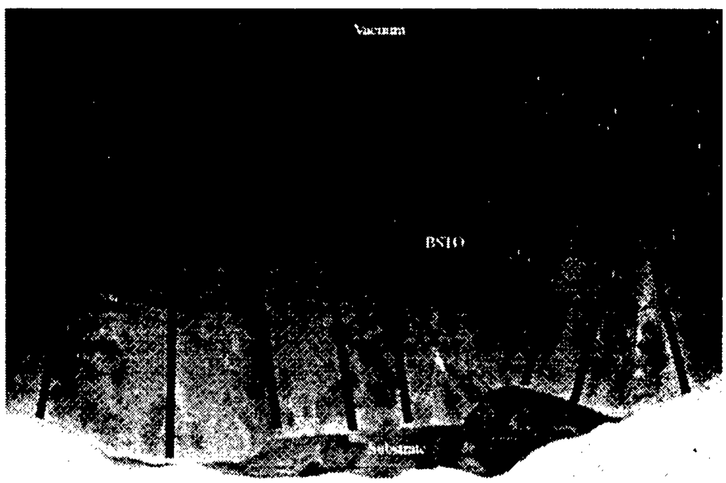

Figure 2. Transmission Electron Micrograph of BSTO Film Illustrating Columnar Grain Structure. Note That the Dark Lines Are Added to Aid in Delineating the Columnar Grain Boundaries ($T_s/T_m = 0.49$).

presented by Movchan and Demchishin (1969). They proposed three zones to describe the microstructures that can develop in films produced by vacuum evaporation as a function of T_s/T_m, where T_s is the absolute substrate temperature and T_m is the absolute melting temperature of the deposited material. Thornton (1977) elaborated on the approach of Movchan and Demchishin (1969) extending it to typical sputtering. Thornton (1977) also concluded that the structure and physical properties of films produced by sputtering could be represented as a function of T_s/T_m, in terms of four zones as shown in Figure 3, each with its own characteristic structure and physical properties. The general features of Thornton's model (1977) were based on the examination of 25- to 250-μm-thick coatings deposited at argon pressures of 1.33 x 10^{-4} (1 mtorr) to 3.9 x 10^{-4} Pa (30 mtorr), using cylindrical-post and hollow-cathode magnetron sputtering sources. Fountzoulas and Nowak (1991) further elaborated on the approach of Movchan et al. (1969) and Thornton (1977), extending them to ion plating. SAED was performed to confirm the crystalline structure of the films. The SAED image showed rings that are indicative of a polycrytstalline film.

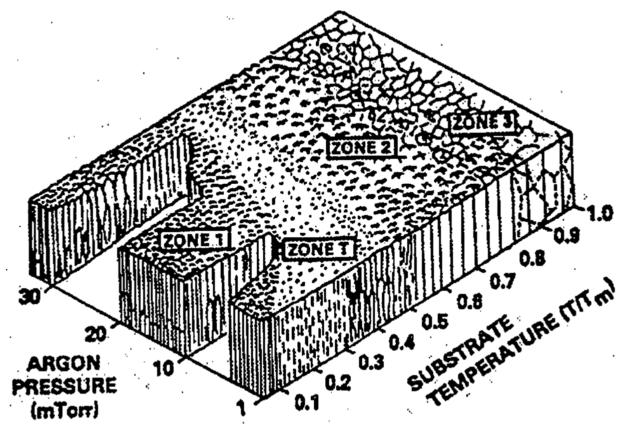

Figure 3. Structure **Zone Model for Coatings Produced by Sputtering (Thornton 1977).**

The column size measurements as a function of the ratio of the absolute substrate temperature, T_s, and absolute film melting temperature, T_m, (2,004 K) are shown in Table 1 and Figure 4. For T_s/T_m between 0.15 and 0.19, the average column diameter increased from 190 nm to 230 nm. For T_s/T_m between 0.19 and 0.39, the average column size remained practically constant At T_s/T_m = 0.49, where the film is fully crystalline, the column size increased dramatically to 2,007 nm. The increased column diameter can be attributed to the increase of intercolumnar diffusion at higher temperatures.

Table 1. Column Diameter, Cohesion, and Adhesion Failure Load and Knoop Microhardness of BSTO Films vs. T_s/T_m

T_s/T_m	Thickness (nm)	Column Size (nm)	L_A (N) (Adhesion Load)	L_C (N) (Cohesion Load)	Knoop Microhardness (GPa)
0.15	1,000	190	16.06	11.63	1.3
0.19	2,200	230	18.75	13.75	1.5
0.29	1,000	250	38.22	13.65	5.7
0.39	1,000	220	22.68	12.96	6.6
0.49	3.000	2.007	24.08	12.32	7.0

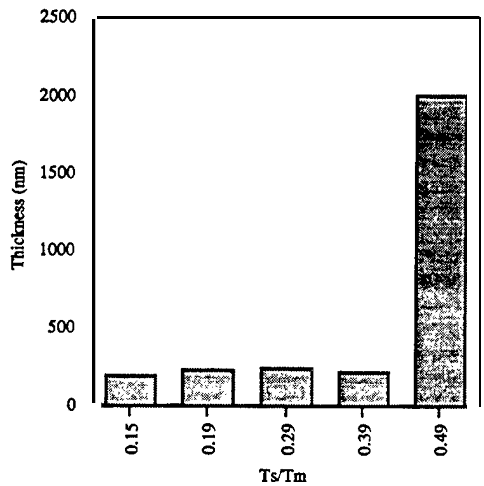

Figure 4. Column Size of BSTO Films vs. T_s/T_m.

The Knoop microhardness of the BSTO films, uncorrected for the substrate hardness effect, ranged between 1.3 GPa and 7 GPa. Table 1 and Figure 5 show Knoop microhardness values as a function of T_s/T_m. The film microhardness increased with an increasing T_s/T_m ratio and increasing film crystallinity. The highest Knoop microhardness was obtained at the highest temperature (i.e., $T_s/T_m = 0.49$).

Measured average values of cohesion failure load, L_C, and adhesion failure load, L_A, are listed in Table 1. The cohesion failure load of the films remained fairly constant, independent of

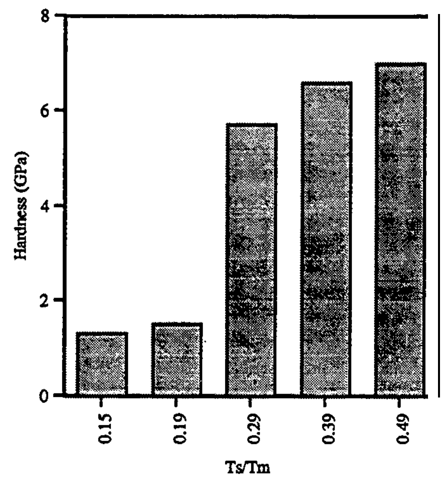

Figure 5. Knoop Microhardness of BSTO films vs. T_s/T_m

the substrate temperature (Figure **6). The** average cohesion failure load of the film was about 13 N. The adhesion failure load of the films increased with increasing T_s/T_m ratio (Figure 7). However, for reasons currently not understood, for T_s/T_m = 0.25, the adhesion failure load exhibited a peak at a ratio of 38.22 N.

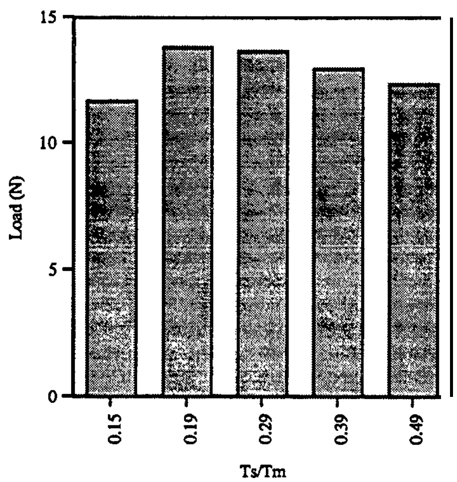

Figure 6. Cohesion Failure Load of BSTO Films vs. T_s/T_m.

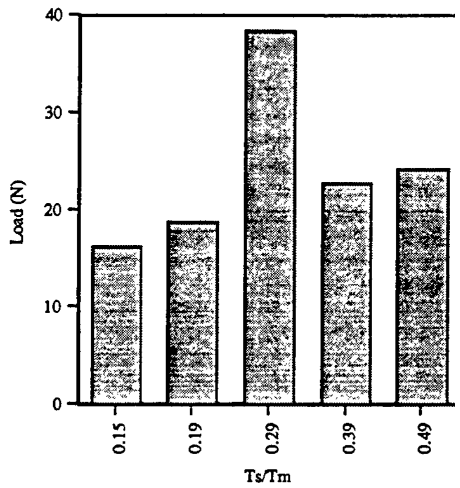

Figure 7. Adhesion Failure Load of BSTO films vs. T_s/T_m.

4. Summary

The structure, crystallinity, cohesion and adhesion failure loads and microhardness of BSTO thin films produced by PLD were correlated with the substrate temperature. For the entire temperature range, 278-973 K, the films were columnar. The column size increased with increasing substrate temperature. For $T_s/T_m \leq 0.29$, the films could be categorized as being in the transition region, T, of the Thornton structural zone model. When $T_s/T_m > 0.29$, the microstructure corresponds to the Thornton structural zone 2 category. SAED confirmed the crystalline nature of the films deposited on the electroded substrates at a temperature of 973 K. The cohesion failure load was constant for the entire substrate temperature range. The adhesion and microhardness increased with increasing substrate temperature.

5. References

Bhansali, K. J., and T. Z. Kattamis. "Quality Evaluation of Coatings by Automatic Scratch Testing." ***Wear,*** vol. 141, p. 59, 1990.

Cole, M. W., S. Sengupta, S. Stowell, C. W. Hubbard, and E. Ngo. 'The Influence of Microstructure on the Electronic Properties of Thin Films of Barium Strontium Titanium Oxide Composites." ***Journal of Integrated Ferroelectrics,*** vol. 21, pp. 469–473, 1998.

Fountzoulas, C., and W. B. Nowak. "Influence of Ion Energy and Substrate Temperature on Structure of Copper, Germanium, and Zinc Films Produced by Ion Plating." ***Journal of Vacuum Science and Technology,*** vol. A9, no. 4, p. 2128, July/August 1991.

Garsgin, A., Y. Lavernova, and E. Mokhov. "Influence of Impurities and Intrinsic Defects on Physicomechanical Properties of Silicon Carbide Single Crystals." ***Ceramics International,*** vol. 23, p. 409, 1997.

lkawa, H. ***Ceramic Transactions.*** Vol. 32, p. 19, 1993.

Kattamis, T. Z. "On the Evaluation of Adhesion of Coatings by Automatic Scratch Testing." ***Journal of Adhesion Science and Technology,*** vol. 7, p. 783, 1993.

Kattamis, T. Z., K. J. Bhansali, M. Levy, R. Adler, and S. Ramalingam. "Evaluation of the Strength and Adherence of Soft Cobalt-Base and Hard Tin Coatings on 4340 Low-Alloy Steel." ***Material Science Engineering, vol. A161,*** p. 105, 1993.

Movchan, A., and S. V. Demchishin. ***Physical Met. Metallogr.*** Vol. 28, p. 653, 1969.

Sengupta, L. C., S. Stowell, E. Ngo, M. E. O'Day, and R. Lancto. "Barium Strontium Titanate and Non-Ferrous Oxide Ceramic Composites for Use in Phased-Array Antennas." ***Integrated Ferroelectrics,*** vol. 8, pp. 77–88, 1995.

Sengupta, S., D. P. Vijay, L. C. Sengupta, and S. B. Desu. "Investigation of Characteristics of Ferroelectric Thin Films Deposited by Pulsed Laser Ablation." MRS Symposium on Smart Materials, vol. 36, p. 545, 1995.

Sengupta, S., L. C. Sengupta, D. P. Vijay, and S. B. Desu. "Thin Films of Novel Ferroelectric Composites." ***Journal of Integrated Ferroelectrics,*** vol. 13, pp. 239-245, 1996.

Steinmann, A., Y. Tardy, and H. E. Hintermann. ***Thin Solid Films.*** Vol. 154, p. 333, 1987.

Thornton, J. A. ***Annual Review of Material Science.*** TA401-A7, vol. 7, p. 239, 1977.

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REPORT DOCUMENTATION PAGE

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. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	April 1999	Final, Sep 97 - Jan 98

. TITLE AND SUBTITLE
Mechanical and Microstructural Evaluation of Barium Strontium Titinate Thin Films for Improved Antenna Performance and Reliability

5. FUNDING NUMBERS
AH84

. AUTHOR(S)
C. W. Hubbard, C. G. Fountzoulas, M. W. Cole, and S. Sengupta

. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: AMSRL-WM-MC
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8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-1930

). SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
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12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

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14. SUBJECT TERMS
thin film, BSTO, ferroelectrics, phased-array antennas, microstructure, mechanical properties

15. NUMBER OF PAGES
15

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	lb SECURITY CLASSIRCATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
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